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## Patent Abstracts of Japan

PUBLICATION NUMBER : 07088355  
PUBLICATION DATE : 04-04-95

APPLICATION DATE : 20-09-93  
APPLICATION NUMBER : 05256432

APPLICANT : TOAGOSEI CO LTD;

INVENTOR : ISOBE YASUSHI;

INT.CL. : B01J 13/04 B01J 13/02 C08K 9/02 C08L101/00

TITLE : MICROCAPSULE

ABSTRACT : PURPOSE: To form an org. halogen compd. into a microcapsule and to remote the reforming or curing of a resin composition by using a film consisting of a fine-grain org. polymer carrying an inorg. fine grain on the surface.

CONSTITUTION: The core material of the org. halogen compd., halogenated resin having a functional group or organotin compd. is dispersed in an aq. medium, a coagulant for coagulating a fine-grain org. polymer, especially a positively charged alumina sol, is added, and then the emulsion of an org. polymer carrying an inorg. fine grain on the surface is added in small amts. under strong agitation. A deionizing agent such as an amphoteric ion exchanger is added, as required, agitation is continued, hence a composite film of the org. polymer and inorg. fine grain is formed on the core material, and a microcapsule slurry is obtained. The microcapsule is excellent in compatibility with resin and dispersibility, and the toxicity, corrosiveness or chemical reaction acceleration of the org. halogen compd., etc., as the core material are retarded.

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- 1995-166531 [22]
- Microcapsules of good dispersibility useful as curing promoter - consist of ~~organic halide or organic tin cpds. coated with inorganic particle loaded organic polymer~~
- JP7088355 The microcapsules consist of cores of organic halide, halogenated resin with functional gps., or organic tin cpds.. They are coated with organic polymer fine particles which are loaded with inorganic fine particles.
- USE/ADVANTAGE - As a curing promoter, a polymerisation catalyst, or a flame retarder additive for plastics or plastics composite. The new microcapsules have good dispersibility and solubility to plastics.
- In an example, 'Snowtex UP'(RTM: colloidal silica sol) was added to an emulsion contg. butylacrylate-butadiene copolymer particles with styrene-acrylonitrile copolymer shells contg. silanol gps. to obtain dispersion (A). 'BREN-S'(RTM: brominated epoxy resin) and 'Aluminasol 200'(RTM) were mixed to obtain dispersion (B). Dispersions (A) and (B) were mixed. Sb203 powder and ion exchange resin beads were added to the mixt.. It was filtered. The resultant filtrate was spray-dried to obtain microcapsules consisting of 3-10 micron dia. cores of brominated epoxy resin which were coated with a composite of butadiene copolymer, silica, alumina, and Sb2O3.(Dwg.0/0)
- MICROCAPSULE DISPERSE USEFUL CURE PROMOTE CONSIST ORGANIC HALIDE ORGANIC TIN COMPOUND COATING INORGANIC PARTICLE LOAD ORGANIC POLYMER
- JP7088355 A 19950404 DW199522 B01J13/04 005pp
- B01J13/02 ; B01J13/04 ; C08K9/02 ; C08L101/00
- A02-A00A A08-C01 A08-D01 A08-F01 A12-W05
- A32 A60
- (TOAG ) TOA GOSEI CHEM IND LTD
- JP19930256432 19930920
- JP19930256432 19930920
  
- JP7088355 A 19950404
- MICROCAPSULE
- PURPOSE: To form an org. halogen compd. into a microcapsule and to remote the reforming or curing of a resin composition by using a film consisting of a fine-grain org. polymer carrying an inorg. fine grain on the surface.
- CONSTITUTION: The core material of the org. halogen compd., halogenated resin having a functional group or organotin compd. is dispersed in an aq. medium, a coagulant for coagulating a fine-grain org. polymer, especially a positively charged alumina sol, is added, and then the emulsion of an org. polymer carrying an inorg. fine grain on the surface is added in small amts. under strong agitation. A deionizing agent such as an amphoteric ion exchanger is added, as required, agitation is continued, hence a composite film of the org. polymer and inorg. fine grain is formed on the core material, and a microcapsule slurry is obtained. The microcapsule is excellent in compatibility with resin and dispersibility, and the toxicity, corrosiveness or chemical reaction acceleration of the org. halogen compd., etc., as the core material are retarded.
- B01J13/04 ; B01J13/02 ; C08K9/02 ; C08L101/00
- TOAGOSEI CO LTD
- ISOBAYASUSHI
- 19950831
- 199507
- JP19930256432 19930920

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(21)Application number : 05-256432

(71)Applicant : TOAGOSEI CO LTD

(22)Date of filing : 20.09.1993

(72)Inventor : ISOBE YASUSHI

## (54) MICROCAPSULE

## (57)Abstract:

PURPOSE: To form an org. halogen compd. into a microcapsule and to remote the reforming or curing of a resin composition by using a film consisting of a fine-grain org. polymer carrying an inorg. fine grain on the surface.

CONSTITUTION: The core material of the org. halogen compd., halogenated resin having a functional group or organotin compd. is dispersed in an aq. medium, a coagulant for coagulating a fine-grain org. polymer, especially a positively charged alumina sol, is added, and then the emulsion of an org. polymer carrying an inorg. fine grain on the surface is added in small amts. under strong agitation. A deionizing agent such as an amphoteric ion exchanger is added, as required, agitation is continued, hence a composite film of the org. polymer and inorg. fine grain is formed on the core material, and a microcapsule slurry is obtained. The microcapsule is excellent in compatibility with resin and dispersibility, and the toxicity, corrosiveness or chemical reaction acceleration of the org. halogen compd., etc., as the core material are retarded.

## LEGAL STATUS

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[Date of final disposal for application]

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**CLAIMS**

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[Claim(s)]

[Claim 1] The microcapsule object which has the coat which consists of the aggregate of the particle-like organic polymer which made the core material the halogenation resin or the organic tin compound which has an organic halogenated compound and a functional group, and supported the minerals particle on the front face.

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[Translation done.]

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**DETAILED DESCRIPTION****[Detailed Description of the Invention]**

**[0001]**

**[Industrial Application]** This invention relates to the microcapsule object which connotes the halogenation resin or the organic tin compound ("an organic halogenated compound etc. is called" hereafter.) which has an organic halogenated compound and a functional group. The microcapsule object of this invention is suitably used as a compounding agent aiming at refining of resin or a resin constituent ("resin" is only called hereafter.), or acceleration of hardening.

**[0002]**

**[Description of the Prior Art]** Combination of a di-n-butyl tin JIRAU rate is tried as a curing agent of the bromination epoxy resin for raising combination of an organic halogenated compound etc., for example, fire retardancy, for the purpose of refining of resin etc., or silicone resin.

**[0003]** However, generally, since the compatibility and dispersibility over resin are remarkable, and an organic halogenated compound etc. is bad, these compounds etc. have large reactivity and it is difficult to control, it has the fault that the handling on processing is difficult and produces an uneven reaction in resin. Furthermore, even if it has blended well into metaphor resin, these compounds had many toxic and corrosive big things, and it needed to prevent emitting easily from resin under the usual environment.

**[0004]** Manufacture of the microcapsule object which generally cannot distribute an organic halogenated compound etc. easily in the shape of impalpable powder underwater since water repellence is high, and connotes these compounds etc. on the other hand was difficult. Moreover, even if oleophilic was large as for many, such as these compounds, and it succeeded in metaphor capsulation, in usual wall membrane, it permeates easily, there is a problem that it is emitted outside, and the microcapsule object which connotes these compounds substantially was not acquired.

**[0005]**

**[Problem(s) to be Solved by the Invention]** Since it was difficult for compatibility and dispersibility when the technical problem which it is going to solve blends an organic halogenated compound etc. with resin to be bad, and to control a reaction, it is easy to produce an uneven reaction, and even if it blends with metaphor resin, from resin, I hear that these compounds are easily emitted to that the handling on a process of processing is difficult, and a list, and they are in them.

**[0006]**

**[Means for Solving the Problem]** this invention person came to complete header this invention for the ability of an organic halogenated compound etc. to be microencapsulated by using the coat which consists of the aggregate of the particle-like organic polymer which supported the minerals particle on the front face, as a result of inquiring wholeheartedly that the above-mentioned technical problem should be solved.

**[0007]** The technical element of the microcapsule object of this invention is explained below.

(1) Although the thermoplastics and thermosetting resin which were known conventionally can be used as an organic polymer used by organic polymer this invention, what is emulsified easily underwater is desirable. As such an organic polymer, acrylonitrile-butadiene rubber, acrylic rubber, styrene-butadiene-rubber, or ethylene-vinyl acetate rubber; or vinyl chloride system resin, vinylidene-chloride system resin, fluorine system resin, a silicone polymer, or a styrene-acrylic-acid copolymer is mentioned, for example.

**[0008]** The particle-like organic polymer which supported the minerals particle on the front face can carry out the emulsion polymerization of the monomer which constitutes for example, the above-mentioned organic polymer by the usual approach, can make the front face of the obtained particle-like organic polymer able to support a minerals particle, and can be obtained. Under the present circumstances, it is required to have affinity sufficient between the front face of a particle-like polymer and a minerals particle. For example, in order to make the front face of a particle-like polymer

support colloidal silica as a minerals particle, it is needed for the front face of a particle-like polymer to make a silanol group exist. Although there are various processes of the particle-like organic polymer which denatured the front face as mentioned above, what was obtained by the core shell mold emulsion polymerization method has the high stability in an emulsification condition, and its membrane formation nature at the time of being capsulation is well desirable.

[0009] A core shell mold emulsion polymerization method generates the emulsion of the organic polymer which serves as a core beforehand, and next, in this emulsion, copolymerization of the monomer which is the raw material of the polymer used as shell can be added and carried out, and it can obtain it. As a surfactant used for generation of the emulsion of the organic polymer used as a core, when the derivative of an anion system surfactant especially sulfonic-acid sodium, or a sodium sulfate is used, molecular weight can obtain an organic large polymer and is desirable. Moreover, the particle size of the organic polymer used as a core has desirable 0.05-1.0 micrometers. Moreover, as for the organic polymer component used as a core, it is desirable to be contained ten to 90% of the weight of the core shell mold polymers obtained, and it is 50 - 90 % of the weight more preferably. At less than 10 % of the weight, when it considers as the coat of a microcapsule object, the property of the organic polymer itself is not demonstrated enough and is not desirable.

[0010] Alkoxysilane which has \*\* acrylonitrile, a methacrylonitrile, N-vinyl pyrrolidone or an N-vinyl caprolactam;\*\* acrylic oxy-radical, a metacryloxy radical, or a vinyloxy radical as a monomer which is the raw material of the polymer used as shell; it is [ that the stable emulsion of a polymer particle is easy to be formed ] desirable when it uses for a list combining three components of the monomer which has other vinyl groups, such as \*\* styrene, vinyltoluene, methyl (meta) acrylate, or ethyl (meta) acrylate.

[0011] As an example of the alkoxysilane which has an acrylic oxy-radical, a metacryloxy radical, or a vinyloxy radical, gamma-acrylic oxy-propyltrimethoxysilane, gamma-methacryloxypropyltrimethoxysilane, gamma-(meta) acrylic oxy-propyl tris (trimethylsiloxy) silane, vinyltrimethoxysilane, a vinyl tris (methoxyethoxy) silane, or vinyl trichlorosilane is mentioned.

[0012] As other manufacture approaches of a particle-like organic polymer of having denatured the front face, the emulsion of an organic polymer is generated and there is a method of making a silane system coupling agent, a titanate system coupling agent, or an aluminum system silane coupling agent add and react to this.

[0013] (2) The following [ 50mmicro ] have a desirable path, and since it is easy to support the minerals particle used by minerals particle this invention on the front face of the particle-like organic polymer which denatured the aforementioned front face as it is the gestalt of the colloid which made ultrafine particle-like powder distribute underwater, it is still more desirable. As such a minerals particle, colloidal silica, alumina sol, a zirconia sol, an antimony oxide sol, a tin-oxide sol, and a path are mentioned for a silica or alumina powder not more than 50mmicro etc.

[0014] The approach of making the front face of the particle-like organic polymer which denatured the front face supporting a minerals particle has the desirable approach of making a direct or drainage system medium distribute the aforementioned minerals particle, and adding gradually under stirring in the aforementioned organic polymer emulsion. Under the present circumstances, since support will be easily performed if a system is warmed at 40-60 degrees C, it is desirable.

[0015] Although the concomitant use rate of an organic polymer emulsion and a minerals particle is adjusted according to the property for which the coat of the last microcapsule object is asked, it is 20 - 90 % of the weight generally [ that 2 - 98% of the weight of the total quantity of the organic polymerization body constituent in an emulsion and a minerals component is an organic polymerization body constituent ], and preferably. At less than 2 % of the weight, if the engine performance of the organic polymer in a coat does not appear but it exceeds 98 % of the weight, the dispersibility of a particle-like organic polymer worsens and is not desirable at the time of microencapsulation.

[0016] In the case of an adhesive organic high polymer, it can be checked by making a film form from the organic polymer emulsion before and behind minerals particle support, and measuring a sharp reduction of the adhesiveness that the minerals particle has been supported by the front face of a particle-like organic polymer.

[0017] (3) The halogenation resin which has functional groups, such as a fluororesin which has the compound; functional group which has a fluorine, chlorine, a bromine, or iodine in intramolecular as an organic halogenated compound used as a core material by core material this invention, or a bromination epoxy resin, or its precursor; esterification tin compounds, such as alkylation tin compounds, such as tetrabutyltin, and a dibutyl tin JIRAU rate, are mentioned. The matter used as these core materials will not ask a liquefied object or powder, if it becomes particle-like in a drainage system medium.

[0018] The liquefied object with the small solubility to water can be used in a drainage system medium, making it able to distribute in the shape of a particle drop. Since its dispersibility is bad when the powdered compound with small

solubility to water is directly added to a drainage system medium at a capsulation process Or grinding processing is carried out. this compound -- once -- the inside of media, such as a basic sol or water glass, -- or [ in addition, / kneading this ] -- If the thing which made the interior distribute this compound in the shape of a particle is obtained and this is added in a drainage system medium at a capsulation process, this compound can be easily distributed in the shape of impalpable powder in a drainage system medium. After making it specifically distribute in alumina sol, water glass, or a lactic-acid aluminum sol, it can atomize by carrying out kneading processing with a ball mill. Under the present circumstances, the alumina sol which carried out electrification to the positivity also has the operation as a flocculant which makes the particle-like organic polymers charged in negative solidify in a capsulation process.

[0019] (4) Distribute the core material of the capsulation approach above in an aquosity medium, and add the emulsion of the organic polymer which added the flocculant which makes a particle-like organic polymer condense, and the alumina sol which carried out electrification and supported the minerals particle to the positivity on the front face under high stirring continuously preferably especially small quantity every.

[0020] If deionization agents, such as a dipolar ion exchanger, are added if needed and stirring is continued, the compound coat of an organic polymer and a non-subtlety particle will be formed in a core material, and a microcapsule object slurry will be obtained. Under the present circumstances, it is better to warm, when the membrane formation temperature of an organic polymer is high. Since the activity of a deionization agent can remove an elution nature ion compound from near the interface of the core material and coat of the generated slurry-like capsule object while formation of a compound coat advances gradually and capsulation becomes easy, elution of the core material from a capsule object can prevent further, and is a desirable approach.

[0021] the above-mentioned slurry-like capsule -- when particle-like antimony oxide is made to exist in the inside of the body, the dust explosion of the acquired impalpable powder-like capsule object can be prevented, and it is handling top insurance.

[0022] If it applies to a spray drying machine after filtering this slurry and removing coarse grain, an impalpable powder-like microcapsule object will be acquired.

[0023]

[Function] Making the emulsion of the organic polymer which supported the minerals particle on the front face condense using a flocculant, a core material is encapsulated, it is acquired and the microcapsule object of this invention was able to acquire the practical capsule object which will not make an organic halogenated compound etc. a core material without this approach. Moreover, since the microcapsule object of this invention has covered the organic halogenated compound etc. by the precise compound coat which consists of minerals and an organic polymer, it distributes easily in other resin by this, and osmosis and elution of a core material are prevented.

[0024]

[Example] Hereafter, an example is given and this invention is explained in more detail.

Example 1 (silanol group) To the autoclave made from stainless steel of the 2l. content volume of composition of the core shell mold emulsion which it has 1000 cc of pure water, and REBENORU WZ (the 26-% of the weight water solution of a polyoxyethylene-alkyl-phenyl-ether sodium sulfate --) 19.2by Kao Corp. g, 2.5g [ of potassium persulfate ], and 3rd class dodecyl mercaptan 1.0g, Butyl acrylate 250g and butadiene 250g are taught. With propeller mold stirring aerofoils Under stirring of 350rpm, A reaction is performed at 50 degrees C for 15 hours. After that REBENORU WZ19.2g, 0.5g [ of potassium persulfate ] and styrene 60g, acrylonitrile 30g, and NUC silane monomer A-171 (vinyltrimetoxysilane, Nippon Unicar make) 10g were taught, and the emulsion polymerization was continued at 70 more degrees C for 5 hours.

[0025] The obtained emulsion used butyl acrylate / butadiene copolymer rubber particle as the core, the styrene/acrylonitrile copolymer which has a silanol group into a shell part were formed, and solid content was 36 % of the weight.

[0026] (Preparation of the particle-like dispersion liquid of a bromination epoxy resin) Bromination epoxy resin BREN-S(weight-per-epoxy-equivalent 285g/eq., 35.3 % of the weight [ of bromine contents ], 83.5 degrees-C [ of softening temperatures ], Nippon Kayaku Co., Ltd. make) 400g and alumina sol 200 (alumina sol [ of particle-size 30-100mmicro which carried out electrification to the positivity ], 10 % of the weight [ of concentration ], Nissan Chemical Industries, Ltd. make) 1000g were taught into the 5l. magnetism ball mill, wet grinding was carried out in bottom of room temperature 300rpm for 12 hours, and dispersion liquid were obtained.

[0027] (Support of a minerals particle) organic polymer emulsion 660g which has a silanol group on the surface of the above -- a 1l. beaker -- teaching -- a propeller mold stirring aerofoil -- as the bottom of stirring of 200rpm, and a defoaming agent -- 2,4,7,9-tetra-methyl-5-decyne-4,7-diol [ ] -- 2g -- adding -- a degree -- the Snow tex UP (hydrosol of the colloid silica of the long and slender configuration of 20 % of the weight of solid content, path 5-20mmicro, and die-



length 40-300mmicro.) the Nissan Chemical Industries, Ltd. make -- preparation liquid was obtained for stirring continuously [ 230g was added gradually and / 40-45 degrees C / for 1 hour ].

[0028] (Composition of a microcapsule object) 650g of particle-like dispersion liquid of 5.8l. of pure water and the above-mentioned bromination epoxy resin was taught to the 12l. mixing chamber, and latex polymer 890g which supported the above-mentioned minerals particle with the propeller mold stirring aerofoil on the front face under stirring of 400rpm was added over 1 hour under the room temperature. Next, 610 cc of pure water, 61.4g of 3 oxidization 2 antimony powder of 1.2-1.6 micrometers of mean diameters, ion-exchange resin Amberlite Intermediate-Routing-Node-150 (the cation which has a sulfonic acid and the 4th class amine radical, and hybrid model ion exchanger of an anion.) The shape of a bead with a particle size of 0.40-1.19mm. 280by ORGANO CORP. g was supplied and stirring was continued at 50 degrees C for 3 hours.

[0029] After removing coarse grain through the obtained slurry-like mixture in the filter cloth of 80 meshes, when it let pass and dried to the disk mold spray drying machine as it is, 33 % of the weight of bromination epoxy resins with a particle size of 3-15 micrometers was connoted, and the impalpable powder-like microcapsule object which has 67 % of the weight of compound coats which consist of a butadiene copolymer, a silica, an alumina, and 3 oxidization 2 antimony was acquired. A 500 times as many scanning electron microscope photograph as the particulate structure of this microcapsule is attached.

[0030] (Measurement of the bromine eluted with the hot water of a capsule object) The seal of obtained 1.0g of capsule objects and 40 cc of pure water was prepared and carried out to the proof-pressure mold wet degradation crucible made from Teflon (a trade name "a uni-seal", the effective cubic capacity of 110 cc, the proof pressure of 350kg/cm2, Acom Make), and heating was continued for 120 degree-Cx 200 hours. After heating, when it cooled to 25 degrees C and the content of the bromine after filtration and in an eluate was measured, the 5 ppm bromine was eluted to the amount of bromination epoxy resins contained in the capsule object concerned.

[0031] When the same experiment was conducted instead of the capsule object concerned using above bromination epoxy resin BREN-S itself (0.33g), the 80 ppm bromine was eluted.

[0032] The capsule object which connotes an example 2 (composition of capsule object which connotes di-n-butyl tin JIRAU rate) di-n-butyl tin JIRAU rate was compounded as follows. Instead of the particle-like dispersion liquid of the bromination epoxy resin used in the example 1, the particle-like dispersion liquid of the following di-n-butyl tin JIRAU rate were prepared. To the mixing chamber of 12l. content volume, they are 5.8l. of pure water, METOROZU 90SH4000 (methoxy hydroxypropylcellulose, Shin-Etsu Chemical Co., Ltd. make) 5.3g, di-n-butyl tin JIRAU rate 186g, and alumina sol 200. 186g was taught, stirring was continued for 30 minutes under stirring of 400rpm with the propeller mold stirring aerofoils under the room temperature, and dispersion liquid were prepared.

[0033] Next, it added to \*\*\*\*, having bet emulsion 890g of the organic polymer which supported the minerals particle obtained in the example 1 on the front face for 5 minutes. Completely like the example 1, subsequent actuation connoted 33 % of the weight of di-n-butyl tin JIRAU rates with a particle size of 5-30 micrometers, and acquired the impalpable powder-like microcapsule object which has 67 % of the weight of compound coats which consist of a butadiene copolymer, a silica, an alumina, and 3 oxidization 2 antimony. A 5000 times as many scanning electron microscope photograph as the particulate structure of this microcapsule is attached.

[0034] (Pot-life assessment as a hardening accelerator to silicone resin) KANEKA When SAIRIRU SAT200 (silicone-acrylic resin, Kaneka Corp. make) 100g, capsule 3.03g (1.0g is connoted as a di-n-butyl tin JIRAU rate) obtained in the example 2, and 0.5g of pure water were taught to the stainless steel container and it mixed for 10 minutes by 2000rpm by DISUPA, the capsule object was distributed finely. Thickening was not accepted although this was left for one week under the room temperature. On the other hand, when heated for 30 minutes at 120 more degrees C, it hardened thoroughly.

[0035] Instead of using an another side this capsule object, di-n-butyl tin JIRAU rate 1.0g was used, and when others were performed like the above, they were almost hardened one day after the bottom of a room temperature.

[0036]

[Effect of the Invention] The microcapsule object of this invention is excellent in the compatibility and dispersibility over resin, and can fully control the toxicity of the organic halogenated compound which is a core material, corrosive, or chemical reaction acceleration nature under the usual environment, and makes the effectiveness as fire retardancy or a polymerization catalyst demonstrate for the first time at the time of the conditions of an activity, for example, an elevated temperature.

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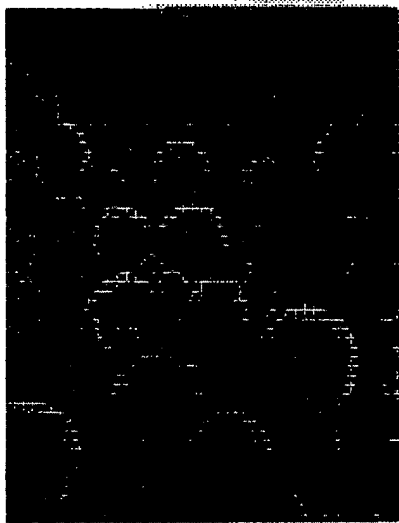
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DRAWINGS

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[Drawing 1]

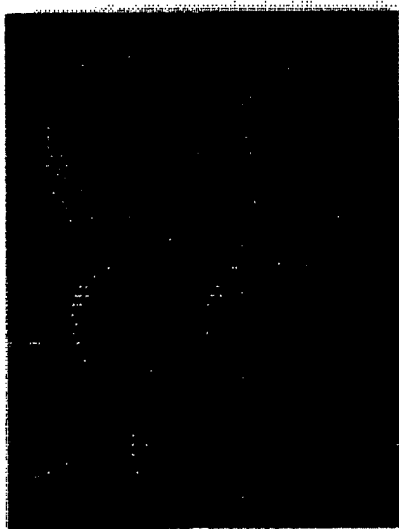
図面代用写真



写真

[Drawing 2]

図面代用写真



写真

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(54) 【発明の名称】 マイクロカプセル体

(57) 【要約】

【構成】 本発明は、有機ハロゲン化合物、官能基を有するハロゲン化樹脂または有機錫化合物を芯材とし、無機質微粒子を表面に担持した微粒子状有機重合体の集合体からなる皮膜を有するマイクロカプセル体。

【効果】 本発明のマイクロカプセル体は、樹脂に対する相溶性および分散性に優れ、また芯材である有機ハロゲン化合物等の毒性、腐食性または化学反応促進性を通常の環境下で十分に抑制することができる。

図面代用写真



写真

#### 【特許請求の範囲】

【請求項1】 有機ハロゲン化合物、官能基を有するハロゲン化樹脂または有機錫化合物を芯材とし、無機質微粒子を表面に担持した微粒子状有機重合体の集合体からなる皮膜を有するマイクロカプセル体。

#### 【発明の詳細な説明】

##### 【0001】

【産業上の利用分野】本発明は、有機ハロゲン化合物、官能基を有するハロゲン化樹脂または有機錫化合物（以下、「有機ハロゲン化合物等」と称する。）を内包するマイクロカプセル体に関するものである。本発明のマイクロカプセル体は、樹脂または樹脂組成物（以下、単に「樹脂」と称する。）の改質または硬化促進を目的とする配合剤として好適に用いられる。

##### 【0002】

【従来の技術】樹脂の改質等を目的に有機ハロゲン化合物等の配合、例えば難燃性を上げるための臭素化エポキシ樹脂またはシリコーン樹脂の硬化剤としてジ-n-ブチル錫ジラウレートとの配合が試みられている。

【0003】しかしながら、一般に有機ハロゲン化合物等は、樹脂に対する相溶性および分散性が著しく悪く、またこれら化合物等は反応性が大きく、かつ制御することは困難であるため、加工上の取扱いが困難で、樹脂中で不均一な反応を生じるという欠点を有する。更に例え樹脂中にうまく配合できたとしても、これら化合物は毒性および腐食性の大きなものが多く、通常的环境下で樹脂から容易に放出することを防止する必要があった。

【0004】一方、有機ハロゲン化合物等は、一般に撥水性が高いため水中に微粉末状に分散し難く、これら化合物等を内包するマイクロカプセル体の製造は困難であった。またこれら化合物等の多くは親油性が大きく、例えばカプセル化に成功したとしても通常の壁膜では容易に浸透し、外部に放出されるという問題があり、実質的にこれら化合物を内包するマイクロカプセル体は得られていなかった。

##### 【0005】

【発明が解決しようとする課題】解決しようとする課題は、有機ハロゲン化合物等は、樹脂に配合した場合の相溶性や分散性が悪く、また反応を制御することが困難であったため、不均一な反応を生じ易く、加工の工程上取扱いが困難であること、並びに、例え樹脂に配合したとしても、これら化合物は、樹脂から容易に放出されるということである。

##### 【0006】

【課題を解決するための手段】本発明者は上記課題を解決すべく鋭意検討した結果、無機質微粒子を表面に担持した微粒子状有機重合体の集合体からなる皮膜を用いることにより、有機ハロゲン化合物等をマイクロカプセル化できることを見出し本発明を完成するに至った。

【0007】本発明のマイクロカプセル体の技術的要素

を以下に説明する。

##### （1）有機重合体

本発明で用いる有機重合体としては、従来知られた熱可塑性樹脂および熱硬化性樹脂を使用できるが、水中で容易に乳化するものが好ましい。このような有機重合体としては、例えばアクリロニトリル-ブタジエンゴム、アクリルゴム、スチレン-ブタジエンゴムまたはエチレン-酢酸ビニルゴム；或いは塩化ビニル系樹脂、塩化ビニリデン系樹脂、フッ素系樹脂、シリコーン重合体またはスチレン-アクリル酸共重合体等が挙げられる。

【0008】無機質微粒子を表面に担持した微粒子状有機重合体は、例えば上記有機重合体を構成する単量体を通常の方法で乳化重合し、得られた微粒子状有機重合体の表面に無機質微粒子を担持させて得ることができる。この際、微粒子状重合体の表面と無機質微粒子間に充分な親和力を有することが必要である。例えば、微粒子状重合体の表面に無機質微粒子としてコロイダルシリカを担持させるためには、微粒子状重合体の表面にシラノール基を存在させることが必要となる。上記のように表面を変性させた微粒子状有機重合体の製法は、種々あるが、コア-シェル型エマルジョン重合法によって得たものは、乳化状態での安定性が高く、またカプセル化の際の成膜性が良く好ましい。

【0009】コア-シェル型エマルジョン重合法は、予めコアとなる有機重合体のエマルジョンを生成し、次に該エマルジョン中に、シェルとなる重合体の原料である単量体を添加し、共重合させて得ることができる。コアとなる有機重合体のエマルジョンの生成のために使用される界面活性剤としては、アニオン系界面活性剤、特にスルホン酸ナトリウムまたは硫酸ナトリウムの誘導体を用いると分子量が大きい有機重合体を得ることができ好ましい。またコアとなる有機重合体の粒径は、0.05～1.0μmが好ましい。またコアとなる有機重合体成分は、得られるコア-シェル型重合体の内、10～90重量%含まれることが好ましく、より好ましくは50～90重量%である。10重量%未満では、マイクロカプセル体の皮膜とした際に有機重合体自体の特性が十分発揮されず好ましくない。

【0010】シェルとなる重合体の原料である単量体としては、①アクリロニトリル、メタクリロニトリル、N-ビニルピロリドンまたはN-ビニルカプロラクタム；②アクリルオキシ基、メタクリルオキシ基またはビニルオキシ基を有するアルコキシシラン；並びに③スチレン、ビニルトルエン、メチル（メタ）アクリレートまたはエチル（メタ）アクリレート等の他のビニル基を有する単量体の3成分を組み合わせて用いると、重合体粒子の安定なエマルジョンが形成され易く好ましい。

【0011】アクリルオキシ基、メタクリルオキシ基またはビニルオキシ基を有するアルコキシシランの具体例としては、γ-アクリルオキシプロピルトリメトキシシ

ラン、γ-メタクリルオキシプロピルトリメトキシシラン、γ-(メタ)アクリルオキシプロピルトリス(トリメチルシロキシ)シラン、ビニルトリメトキシシラン、ビニルトリス(メトキシエトキシ)シランまたはビニルトリクロロシラン等が挙げられる。

【0012】表面を変性させた微粒子状有機重合体の他の製造方法としては、有機重合体のエマルジョンを生成し、これにシラン系カップリング剤、チタネート系カップリング剤またはアルミニウム系シランカップリング剤を添加し反応させる方法がある。

#### 【0013】(2) 無機質微粒子

本発明で用いられる無機質微粒子は、径が50μm以下のものが好ましく、また超微粒子状粉末を水中に分散せしめたコロイド状の形態であると、前記の表面を変性させた微粒子状有機重合体の表面に担持し易いので更に好ましい。このような無機質微粒子としては、コロイダルシリカ、アルミナゾル、ジルコニアゾル、酸化アンチモンゾル、酸化スズゾル、径が50μm以下のシリカまたはアルミナ粉末等が挙げられる。

【0014】表面を変性させた微粒子状有機重合体の表面に無機質微粒子を担持させる方法は、例えば前記の無機質微粒子を直接または水系媒体に分散させて、前記の有機重合体エマルジョン中に攪拌下に徐々に添加する方法が好ましい。この際系を40～60℃に加温すると担持が容易に行われるので好ましい。

【0015】有機重合体エマルジョンと無機質微粒子の併用割合は、最終のマイクロカプセル体の皮膜に求められる特性に応じて調整されるが、エマルジョン中の有機重合体成分と無機質成分の合計量の、2～98重量%が有機重合体成分であるのが一般的であり、好ましくは20～90重量%である。2重量%未満では、皮膜における有機重合体の性能が表れず、98重量%を超えると、マイクロカプセル化時に、微粒子状有機重合体の分散性が悪くなり好ましくない。

【0016】微粒子状有機重合体の表面に無機質微粒子が担持されたことは、例えば粘着性の高い有機重合体の場合には、無機質微粒子担持前後の有機重合体エマルジョンからフィルムを形成させて、その粘着性の大幅な減少を測定することにより、確認することができる。

#### 【0017】(3) 芯材

本発明で芯材として用いられる有機ハロゲン化合物等としては、フッ素、塩素、臭素またはヨウ素を分子内に有する化合物；官能基を有するフッ素樹脂または臭素化エポキシ樹脂等の官能基を有するハロゲン化樹脂またはその前駆体；テトラブチル錫等のアルキル化錫化合物、ジブチル錫ジラウレート等のエステル化錫化合物が挙げられる。これらの芯材として用いられる物質は、水系媒体中で微粒子状となるものならば、液状物または粉末を問わない。

【0018】水に対する溶解度が小さい液状物は、水系

媒体中で微粒子滴状に分散させて使用することができる。水に対する溶解度の小さな粉末状化合物は、カプセル化工程で水系媒体に直接加えると分散性が悪いので、該化合物を一度塩基性ゾルまたは水ガラス等の媒体中に加えて、これを混練するかまたは粉碎処理して、内部に該化合物を微粒子状に分散させたものを得、これをカプセル化工程で水系媒体中に添加すると、該化合物は容易に水系媒体中に微粉末状に分散することができる。具体的にはアルミナゾル、水ガラスまたは乳酸アルミゾル中に分散させた後、ボールミルで混練処理することにより微粒子化することができる。この際、陽性に荷電したアルミナゾルは、カプセル化工程において、負に帯電されている微粒子状有機重合体同士を凝固させる凝集剤としての作用も有する。

#### 【0019】(4) カプセル化方法

上記の芯材を水性媒体中に分散させ、微粒子状有機重合体を凝集させる凝集剤、特に好ましくは陽性に荷電したアルミナゾルを添加し、続いて高攪拌下に、無機質微粒子を表面に担持した有機重合体のエマルジョンを少量ずつ添加する。

【0020】必要に応じて両性イオン交換体等の脱イオン剤を添加して攪拌を続けると、有機重合体と無機微粒子の複合皮膜が芯材に形成され、マイクロカプセル体スラリーが得られる。この際有機重合体の成膜温度が高いときには加温した方がよい。脱イオン剤の使用は、複合皮膜の形成が徐々に進行してカプセル化が容易になると同時に、生成したスラリー状カプセル体の、芯材と皮膜の界面付近から溶出性イオン化合物を除去できるため、カプセル体からの芯材の溶出が更に防止することができ好ましい方法である。

【0021】上記スラリー状カプセル体中に、微粒子状酸化アンチモンを存在させておくと、得られた微粉末状カプセル体の粉塵爆発を防止することができ、取扱上安全である。

【0022】該スラリーをろ過して粗粒子を除いてからスプレー乾燥機にかけると、微粉末状のマイクロカプセル体を得られる。

#### 【0023】

【作用】本発明のマイクロカプセル体は、無機質微粒子を表面に担持した有機重合体のエマルジョンを、凝集剤を用いて凝集させつつ、芯材をカプセル化して得られるもので、この方法により初めて有機ハロゲン化合物等を芯材とする実用的なカプセル体を得ることができた。また本発明のマイクロカプセル体は、有機ハロゲン化合物等を無機質および有機重合体よりなる緻密な複合皮膜で覆っているため、これにより他の樹脂中に容易に分散され、かつ芯材の浸透および溶出が防止されているものである。

#### 【0024】

【実施例】以下、実施例を挙げて、本発明を更に詳しく

説明する。

#### 実施例 1

(シラノール基を有するコア-シェル型エマルジョンの合成) 2リットル内容積のステンレス製オートクレーブに、純水1000cc、レベノールWZ (ポリオキシエチレンアルキルフェニルエーテル硫酸ナトリウムの26重量%水溶液、花王(株)製) 19.2g、過硫酸カリウム2.5g、第3級ドデシルメルカプタン1.0g、ブチルアクリレート250gおよびブタジエン250gを仕込み、プロペラ型攪拌翼で350rpmの攪拌下、50℃にて15時間反応を行い、その後レベノールWZ 19.2g、過硫酸カリウム0.5g、スチレン60g、アクリロニトリル30gおよびNUCシランモノマーA-171 (ビニルトリメトキシシラン、日本ユニカー(株)製) 10gを仕込み、更に70℃で5時間乳化重合を続けた。

【0025】得られたエマルジョンはブチルアクリレート/ブタジエン共重合体ゴム粒子をコアとして、シェル部分にシラノール基を有するスチレン/アクリロニトリル共重合体が形成されたもので、固形分は36重量%であった。

【0026】(臭素化エポキシ樹脂の微粒子状分散液の調製) 臭素化エポキシ樹脂BREN-S (エポキシ当量285g/eq.、臭素含有量35.3重量%、軟化点83.5℃、日本化薬(株)製) 400gとアルミナゾル200 (陽性に荷電した粒径30~100nmのアルミナゾル、濃度10重量%、日産化学工業(株)製) 1000gを5リットル磁性ボールミル中に仕込み、室温下300rpmにて12時間湿式粉碎して分散液を得た。

【0027】(無機質微粒子の担持) 前記の表面にシラノール基を有する有機重合体エマルジョン660gを1リットルビーカーに仕込み、プロペラ型攪拌翼で200rpmの攪拌下、消泡剤として、2, 4, 7, 9-テトラメチル-5-デシン-4, 7ジオール 2gを添加し、次にスノーテックスUP (固形分20重量%、径5~20nm、長さ40~300nmの細長い形状のコロイド状シリカの水性ゾル。日産化学工業(株)製) 230gを徐々に添加して、40~45℃にて1時間攪拌を続けて調製液を得た。

【0028】(マイクロカプセル体の合成) 12リットル混合槽に純水5.8リットルと上記の臭素化エポキシ樹脂の微粒子状分散液650gを仕込み、室温下、プロペラ型攪拌翼で400rpmの攪拌下、上記の無機質微粒子を表面に担持したラテックスポリマー890gを1時間かけて添加した。次に純水610cc、平均粒径1.2~1.6μmの三酸化二アンチモン粉末61.4gおよびイオン交換樹脂アンバーライトIRN-150 (スルホン酸および第4級アミン基を有するカチオンおよびアニオンの混合型イオン交換体。粒径0.40~

1.19mmのビーズ状。オルガノ(株)製) 280gを投入して50℃にて3時間攪拌を続けた。

【0029】得られたスラリー状混合物を80メッシュのろ布に通して粗粒子を除去した後、そのままディスク型スプレー乾燥機に通して乾燥したところ、粒径3~15μmの臭素化エポキシ樹脂33重量%を内包し、ブタジエン共重合体、シリカ、アルミナおよび三酸化二アンチモンよりなる複合皮膜67重量%を有する微粉末状マイクロカプセル体を得た。このマイクロカプセルの粒子構造の5000倍の走査型電子顕微鏡写真を添付する。

【0030】(カプセル体の熱水により溶出される臭素の測定) 得られたカプセル体1.0gと純水40ccをテフロン製耐圧型湿式分解ルツボ(商品名「ユニシール」、実容積110cc、耐圧350kg/cm<sup>2</sup>、(株)アコム製)に仕込み、シールし、120℃×200時間加熱を続けた。加熱後、25℃まで冷却して濾過後、溶出液中の臭素の含有量を測定したところ、当該カプセル体に含まれる臭素化エポキシ樹脂量に対して5ppmの臭素が溶出していた。

【0031】当該カプセル体の代わりに上記の臭素化エポキシ樹脂BREN-Sそのものを用いて(0.33g)、同様な実験を行ったところ、80ppmの臭素が溶出した。

#### 【0032】実施例 2

(ジn-ブチル錫ジラウレートを含むカプセル体の合成) ジn-ブチル錫ジラウレートを含むカプセル体を次のようにして合成した。実施例1で用いた臭素化エポキシ樹脂の微粒子状分散液の代わりに、次のジn-ブチル錫ジラウレートの微粒子状分散液を調製した。12リットル内容積の混合槽に、純水5.8リットル、メトローズ90SH4000 (メトキシヒドロキシプロピルセルロース、信越化学工業(株)製) 5.3g、ジn-ブチル錫ジラウレート186gおよびアルミナゾル200 186gを仕込み、室温下、プロペラ型攪拌翼で400rpmの攪拌下、30分間攪拌を続け、分散液を調製した。

【0033】次に、実施例1で得た無機質微粒子を表面に担持した有機重合体のエマルジョン890gを5分間かけて徐々に添加した。以降の操作は実施例1と全く同様にして、粒径5~30μmのジn-ブチル錫ジラウレート33重量%を内包し、ブタジエン共重合体、シリカ、アルミナおよび三酸化二アンチモンよりなる複合皮膜67重量%を有する、微粉末状マイクロカプセル体を得た。このマイクロカプセルの粒子構造の5000倍の走査型電子顕微鏡写真を添付する。

【0034】(シリコーン樹脂に対する硬化促進剤としてのポットライフ評価) カネカ サイリルSAT200 (シリコーン-アクリル樹脂、鐘淵化学工業(株)製) 100g、実施例2で得られたカプセル3.03g (ジn-ブチル錫ジラウレートとして1.0gを内包) およ

び純水0.5gをステンレス容器に仕込み、ディスペー  
で2000rpmにて10分間混合したところ、きれいに  
カプセル体は分散された。これを室温下1週間放置し  
たが増粘は認められなかった。一方、更に120℃で3  
0分間加熱したところ、完全に硬化した。

【0035】他方該カプセル体を使用する代わりに、ジ  
n-ブチル錫ジラウレート1.0gを使用し、他は上記  
と同様に行ったところ、室温下1日後には殆ど硬化して  
いた。

【0036】

【発明の効果】本発明のマイクロカプセル体は、樹脂に

対する相溶性および分散性に優れ、また芯材である有機  
ハロゲン化合物等の毒性、腐食性または化学反応促進性  
を通常的环境下で十分に抑制することができ、使用の条  
件、例えば高温時において、難燃性または重合触媒とし  
ての効果を初めて発揮せしめるものである。

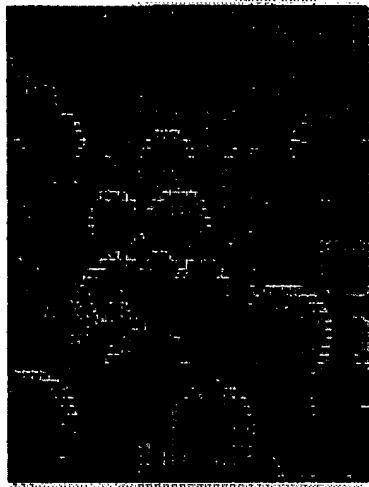
【図面の簡単な説明】

【図1】実施例1で得たマイクロカプセルの粒子構造の  
500倍の走査型電子顕微鏡写真である。

【図2】実施例2で得たマイクロカプセルの粒子構造の  
5000倍の走査型電子顕微鏡写真である。

【図1】

図面代用写真



写真

【図2】

図面代用写真



写真

フロントページの続き

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